Determination of the width of the carrier recombination zone in organic light-emitting diodes

J. Kalinowski[a)]
Department of Molecular Physics, Technical University of Gdańsk, ulisa G. Narutowicza 11/12, 80-952 Gdańsk, Poland

L. C. Palilis,[b)] W. H. Kim,[b)] and Z. H. Kafafi[c)]
U.S. Naval Research Laboratory, Washington, D.C. 20375

(Received 29 July 2003; accepted 18 September 2003)

Bilayer organic light-emitting diodes based on tris-(8-hydroxyquinolinato) aluminum III have been fabricated where the thickness of the light-emitting layer was varied between 10 and 80 nm while maintaining a constant total thickness of the organic layers. The electroluminescence quantum efficiency of the devices was measured as a function of the emitter thickness, and used to determine the width of the carrier recombination zone at different electric fields. The width of the carrier recombination zone is found to decrease with an increase in electric field [from 70 nm ($E=0.75$ MV/cm) to 40 nm ($E=1.0$ MV/cm)]. It is also related to the field-dependent carrier injection efficiency. An estimate of the light output coupling factor (0.4) is also given based on this analysis. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1624477]

I. INTRODUCTION

The maximum electroluminescence (EL) quantum efficiency of light generated by the recombination of oppositely charged carriers injected from electrodes in organic light-emitting diodes (LEDs) can be achieved by minimizing the leakage of holes and electrons. This is equivalent to minimizing the carrier recombination to transit time ratio ($\tau_{\mathrm{rec}}/\tau_t$) or the width of the carrier recombination zone (w).[1] This concept led to the development of highly efficient organic LEDs composed of two or more organic layers, where the internal interfaces act as energy barriers accumulating space charge.[2,3] These internal barriers, together with the different charge carrier mobilities, extend the carrier transit time (τ_t), while charge accumulation at the interfaces reduces the carrier recombination time (τ_{rec}) and screens the applied electric field. The resulting decrease in the $\tau_{\mathrm{rec}}/\tau_t$ ratio leads to an increase in the EL quantum efficiency, φ_{EL}. It is often assumed that the carrier recombination probability (P_R) in bilayer organic LEDs is close to unity. Under device operating conditions, $P_R<1$ since $P_R=(1+\tau_{\mathrm{rec}}/\tau_t)^{-1}$ and $P_R \rightarrow 1$ would require $(\tau_{\mathrm{rec}}/\tau_t)\rightarrow 0$. When $1/2<P_R<1$, carrier decay is dominated by their recombination whereas for $P_R<1/2$, leakage of the carriers to the electrodes is dominant. The $\tau_{\mathrm{rec}}/\tau_t$ ratio can be expressed as the ratio of the recombination zone width (w) to the emitter thickness (d_e), which leads to $P_R=(1+w/d_e)^{-1}$.[4,5] In molecular solids, the lower limit for w is dictated by the distance between the closest two molecules ($\cong 2$ nm). The recombination probability may then approach unity ($P_R \cong 0.98$) for a thick emitting film ($d_e \cong 100$ nm) but for a thin one ($d_e \cong 10$ nm), it drops to $P_R=0.83$. Consequently, φ_{EL} will be smaller for thin emitting layers (EMLs) compared to thick EMLs for the same recombination zone width, w. For $w=d_e$, the P_R decreases to 0.5 when the unimolecular and bimolecular decay probabilities of the charge carriers become comparable. To date few attempts have been undertaken to determine the width of the carrier recombination zone.[5–9] They have usually been based on complex methods that involve comparisons between the measured EL and photoluminescence (PL) spectra in single crystals,[6] polymer blends,[7] or Langmuir–Blodgett films.[8] A relatively simple method, based on the definition of φ_{EL}, applied to organic LEDs, assumes (often with no justification) a value of the light output coupling factor (χ) based on the refractive index of the organic layers.[5,9] This factor includes light loss due to waveguide modes that propagate along the internal interfaces as well as the transparent substrate/air interface.[10–12] In this communication, we present a simple method to determine the width of the carrier recombination zone in organic LEDs based on a common structure: indium–tin-oxide (ITO)/N,N'-diphenyl-N,N'-bis(3 methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD)/tris-(8-hydroxyquinolinato) aluminum III (Alq_3)/Mg:Ag. In addition, an independent evaluation of the light output coupling factor is presented.

II. EXPERIMENTAL DETAILS

Bilayer LEDs were prepared by thermal evaporation in vacuum at $\sim 10^{-7}$ Torr. ITO patterned glass substrates were sequentially sonicated in detergent solution, de-ionized water, acetone, and isopropanol, and finally subjected to oxygen plasma treatment for 5 min. TPD, obtained from H. W. Sands, was used as the hole transport layer and Alq_3, obtained from TCI America, was used as the emitting/electron transport layer. TPD was used as received while Alq_3 was purified by train sublimation. A 100 nm thick Mg:Ag film,

a)Electronic mail: kalino@polnet.cc
b)Also at SFA, Inc., Largo, MD 20774; electronic mail: leonidas@ccs.nrl.navy.mil
c)Electronic mail: kafafi@nrl.navy.mil

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2003		**00-00-2003 to 00-00-2003**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Determination of the width of the carrier recombination zone in organic light-emitting diodes	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,4555 Overlook Avenue SW,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**4**	

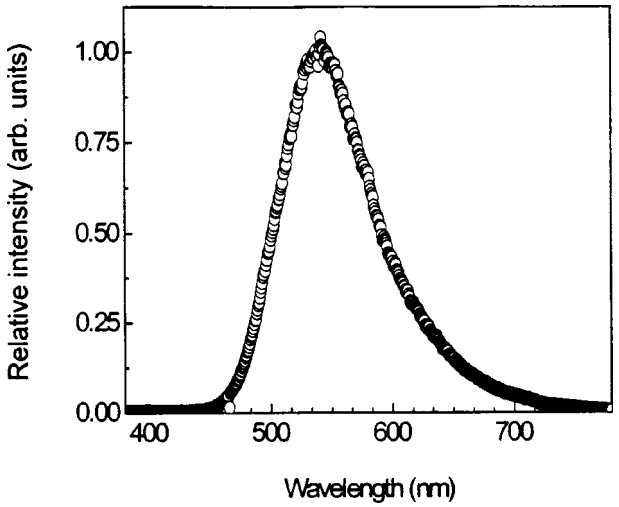

FIG. 1. Typical electroluminescence spectrum of one of the bilayer devices.

prepared by coevaporation of Mg and Ag at a weight ratio of 12 to 1, was used as the cathode. Fourteen different devices with a total organic layer thickness of 120 nm and various TPD and Alq_3 thicknesses were prepared. The Alq_3 layer thickness varied from 10 to 80 nm in steps of 5 nm. The deposition rate was monitored by an *in situ* quartz crystal microbalance and used to estimate the thickness of each of the layers. The deposition rate was 0.2 nm/s for the organics. The total rate of the metal deposition was 0.5 nm/s. The device area was 4 mm^2. All optical and electrical characterization was performed inside a nitrogen-filled glove box. The electroluminescence spectra were recorded with a 1/4 m spectrograph coupled to a charge coupled device (CCD) camera. Current and luminance versus voltage measurements were performed using a Keithley 238 source unit and a Minolta LS-110 luminance meter, respectively.

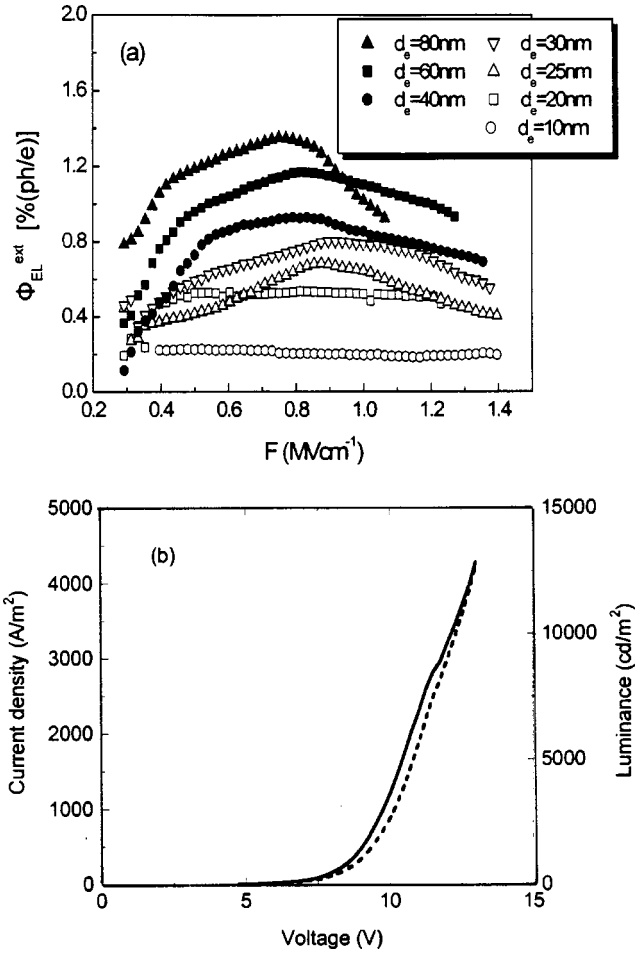

FIG. 2. (a) External EL quantum efficiency as a function of the electric field with varying Alq_3 thicknesses (d_e). (b) Current density (dashed line) and luminance (solid line) vs voltage characteristics of the ITO/TPD (40 nm)/Alq_3 (80 nm)/Mg:Ag device.

III. RESULTS AND DISCUSSION

The EL spectra measured for all the devices with varying Alq_3 (d_e) thicknesses were all similar and characteristic of the PL spectrum of Alq_3 (Fig. 1). Possible microcavity effects[10,11] could, therefore, be neglected in the present analysis. Figure 2(a) shows the external EL quantum efficiency $\varphi_{EL}^{(ext)}$ as a function of electric field measured at various Alq_3 thicknesses. For thin Alq_3 layers ($d_e < 20$ nm) $\varphi_{EL}^{(ext)}$ appears to be field independent, whereas for thicker layers ($d_e > 25$ nm) nonmonotonic evolution of $\varphi_{EL}^{(ext)}$ with the electric field is observed, consistent with previous results.[5] Figure 2(b) shows current and luminance versus voltage characteristics of a bilayer device with a 80 nm Alq_3 layer. The device reaches luminance of $\sim$13 000 cd/m^2 at 13 V and maximum $\varphi_{EL}^{(ext)}$ of 1.35% at 1450 cd/m^2 (at 9 V).

A simple approach is used to determine the emitter thickness dependence of $\varphi_{EL}^{(ext)}$ by examining the evolution of the recombination zone (located inside Alq_3 and adjacent to the interface with TPD) as the τ_{rec}/τ_t ratio increases. By definition, $\varphi_{EL}^{(ext)}$ is given by

$$\varphi_{EL}^{(ext)} = \xi P_S \varphi_r (1 + w/d_e)^{-1}, \tag{1}$$

where the light output coupling factor, ξ, couples $\varphi_{EL}^{(ext)}$ to the internal EL quantum efficiency, φ_{EL}, ($\xi = \varphi_{EL}^{(ext)}/\varphi_{EL}$), P_S is the probability of an electron-hole recombination event producing a singlet exciton, i.e., the production efficiency of singlet excitons, and φ_r is the efficiency of the radiative decay of a singlet exciton, which is not necessarily equal to the PL quantum efficiency (φ_{PL}) since excitons can be quenched by the electric field[1,4,5] and at the organic/cathode interface.[13] Hence the emitter thickness d_e can affect the Alq_3 excited state lifetime. Consequently, $\varphi_{EL}^{(ext)}$ would become a complex function of d_e which may depend on both φ_r and P_R. If one assumes that $\varphi_r(d_e) = \varphi_{PL} = 0.25$,[5] Eq. (1) can be expressed as

$$\frac{1}{\varphi_{EL}^{(ext)}} = A + \frac{B}{d_e}, \tag{2}$$

where $A = (\xi P_S \varphi_{PL})^{-1}$ and $B = Aw$.

A plot of the inverse of $\varphi_{EL}^{(ext)}$ as a function of the inverse of the emitter thickness, d_e, is shown in Fig. 3. At high electric fields, $F \geq 0.75$ MV/cm, the width of the recombination zone is found to vary between 70 (0.75 MV/cm) and 40 nm (1.0 MV/cm).[14] The reduction in the width of the recombination zone with an increase in electric field is consistent

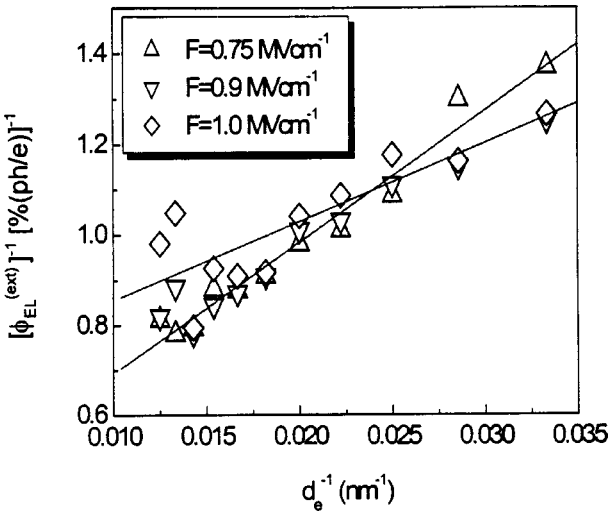

FIG. 3. Inverse of the external EL quantum efficiency as a function of the inverse of the emitter thickness (d_e). The fit of the data (straight solid lines) allows determination of the width of the recombination zone (w) and the light output coupling factor (ξ) at different electric fields (F).

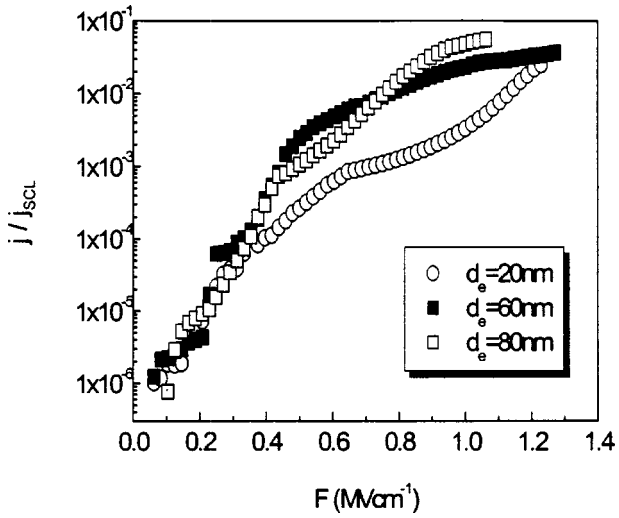

FIG. 4. Carrier injection efficiency, η_{inj} ($\eta_{inj}=j/j_{SCL}$) as a function of the electric field for selected values of Alq_3 thickness.

with previous results[5] and explains the deviation from the $1/d_e$ linear dependence of $[\varphi_{EL}^{(ext)}]^{-1}$ for small emitter thickness and low fields. The width of the recombination zone is by definition the region where all carriers recombine. It is equivalent to the path length the carrier traverses during the recombination time, $w=\mu F \tau_{rec}$, where μ is the mobility and F is the electric field. In the device under study the holes entering Alq_3 recombine on their way to the cathode, so that $\mu=\mu_h$ (hole mobility of Alq_3) and w can vary between its lower limit ($\cong$2 nm, i.e., intermolecular distance in a molecular solid) and beyond the actual thickness of the Alq_3 layer. If at a given electric field w is independent of the emitter thickness (d_e), increasing d_e will simply extend the emitting region with a concomitant increase of $\varphi_{EL}^{(ext)}$. The emitter thickness dependence of $\varphi_{EL}^{(ext)}$ would deviate from that given by Eq. (2). At large Alq_3 thickness, a much stronger increase in $\varphi_{EL}^{(ext)}$ with increasing d_e was observed at low electric fields, $F \leqslant 0.4$ MV cm^{-1}. When the Alq_3 thickness is smaller than the exciton diffusion length in Alq_3, $d_e \leqslant 30$ nm,[13] exciton quenching occurs at the Alq_3/cathode interface, regardless of the field applied, and leads to a decrease in $\varphi_{EL}^{(ext)}$.

One may estimate the value of light output coupling factor ξ from the intercept $[A=(\xi P_S \varphi_{PL})^{-1}]$ of the plots in Fig. 3. If one assumes $\varphi_r=\varphi_{PL}=25\%$ at $F=0.75$ MV/cm and $\varphi_r=17\%$ at $F=1.0$ MV/cm, $\xi \cong 0.43$. This value is twice as large as that obtained assuming $\xi \cong (1/2n^2)$ where n is the refractive index of Alq_3. The efficiency of radiative decay of singlet excitons is assumed to be only 17% at high electric field (1.0 MV/cm) due to $\approx$30% field-induced fluorescence quenching, observed for thick EMLs, as reflected in Fig. 2 for $d_e=80$ nm. The carrier recombination probability, $P_R=(1+w/d_e)^{-1}$,[4,5] can be readily evaluated based on the values of the recombination zone width. A lower and an upper limit, $P_R \cong 0.4$ and $\cong 0.7$, are obtained for $d_e=40$ and 80 nm, respectively. Both are less than the often assumed value of $P_R \cong 1$, and suggest that the devices are operating in the injection limited current regime where the injection efficiency is expected to increase with an increase in voltage. A measure of the carrier injection efficiency, η_{inj}, is the ratio of the actual current (j) to space-charge-limited current (SCLC) (j_{SCL}) ($\eta_{inj}=j/j_{SCL}$).[15] For double-injection current, as in these bilayer devices, the volume-controlled current (VCC) (j_{VCC}), expressed as $j_{VCC}=(9/8)\mu_{eff}\varepsilon_0 \varepsilon F^2/d$, would correspond to single carrier j_{SCL}, since the effective carrier mobility μ_{eff} can be approximated by the hole mobility of TPD.[15] The effective mobility may be approximated by a simple sum of the electron mobility in Alq_3 (μ_e) and hole mobility in TPD (μ_h) in the case of strong recombination. Since TPD is a hole transporting material with $\mu_h \gg \mu_e$, $j_{VCC} \cong j_{SCL}$ for hole injection at the ITO/TPD interface and j_{SCL} may be calculated based on $\mu_{eff} \cong \mu_h \cong 10^{-3}$ cm^2/V s and a dielectric constant $\varepsilon=3$.[16,17] The carrier injection efficiency plotted as a function of the electric field is shown in Fig. 4 where the electric field in TPD resulting from hole accumulation at the TPD/Alq_3 interface has been accounted for using a screening factor $k \cong 0.5$.[1,5] As expected, j is less than j_{SCL} (j does not exceed 0.1 j_{SCL}) for any given electric field. The apparent drop in injection efficiency for a 20 nm thick emitter layer is a direct consequence of the fact that the strong recombination case approximation is not valid for thin EMLs. In this case, the width of the recombination zone exceeds the emitter thickness and the effective mobility μ_{eff} is no longer a simple sum of μ_e (Alq_3) and μ_h (TPD).[18] Nevertheless, a monotonic field increase of the injection efficiency leads to a monotonic increase in the recombination probability (P_R). We note that, in general, the screening factor is a function of the field applied, $k=k(F)$, since the amount of charge accumulated at the TPD/Alq_3 interface varies according to the voltage applied. The assumption that $k(F)=$const has already been shown to be a reasonable approximation for injection-controlled EL on the basis of one-dimensional (1D) Onsager model plots of the injected current versus electric field and thus, we treat it as such here.[5] In an alternative, more exact treatment, 1D Poisson and current continuity equations must be solved to see the influence of

the space-charge distribution on the electric field within the two layers of double-layer LEDs. Its application to organic LEDs has enabled calculation of the spatial distribution of the electric field and charge carrier densities,[19] and to simulate current–voltage characteristics.[20] The results related to SCLC conditions have predicted narrow recombination zones that are located within the electron-transporting/emitting layer near the heterojunction interface as is also expected for the present bilayer LEDs with injection efficiency and thus recombination probability approaching unity.

IV. CONCLUSIONS

In summary, it is shown that the Alq_3 thickness dependence of the EL quantum efficiency of bilayer organic LEDs (ITO/TPD/Alq_3/Mg:Ag) can be directly related to the width of the carrier recombination zone. The device efficiency is influenced by the width of the recombination zone and by the quenching of excited states, and both are electric field dependent. The width of the carrier recombination zone, being a good microscopic device parameter, can also be related to the carrier injection efficiency (η_{inj}), and is shown to decrease as η_{inj} increases with an increase in electric field. The estimated value of 0.43 for the light output coupling factor is a factor of 2 larger than the value of ~ 0.2 widely used in the literature. These results suggest that the theoretical limit for the external EL quantum efficiency based on the simple relationship $\xi \cong (1/2n^2)$ may be underestimated.

ACKNOWLEDGMENTS

Financial support of this work by the Office of Naval Research (ONR) is gratefully acknowledged.

[1] J. Kalinowski, J. Phys. D **32**, R179 (1999).
[2] C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).
[3] C. W. Tang, S. A. Van Slyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989).
[4] J. Kalinowski, P. Di Marco, V. Fattori, L. Giulietti, and M. Cocchi, J. Appl. Phys. **83**, 4242 (1998).
[5] J. Kalinowski, L. C. Picciolo, H. Murata, and Z. H. Kafafi, J. Appl. Phys. **89**, 1866 (2001), and references therein.
[6] J. Kalinowski, Synth. Met. **64**, 123 (1994).
[7] H. Vestweber, H. Bässler, J. Grüner, and R. Friend, Chem. Phys. Lett. **256**, 37 (1996).
[8] J. Grüner, M. Remmers, and D. Neher, Adv. Mater. (Weinheim, Ger.) **9**, 964 (1997).
[9] J. Kalinowski, H. Murata, L. C. Picciolo, and Z. H. Kafafi, J. Phys. D **34**, 3130 (2001).
[10] V. Bulović, V. B. Khalfin, G. Gu, P. E. Burrows, D. Z. Garbuzov, and S. R. Forrest, Phys. Rev. B **58**, 3730 (1998-I).
[11] S. K. So, W. K. Choi, L. M. Leung, and K. Neyts, Appl. Phys. Lett. **74**, 1939 (1999).
[12] M.-H. Lu and J. C. Sturm, J. Appl. Phys. **91**, 595 (2002).
[13] J. Kalinowski, V. Fattori, and P. Di Marco, Chem. Phys. **266**, 85 (2001), and references therein.
[14] The linear fit at low fields (<0.75 MV/cm) does not give a physical meaning to Eq. (2) since it gives a negative value to fit parameter *A* which by definition is positive.
[15] A. Ioannidis, J. S. Facci, and M. A. Abkowitz, J. Appl. Phys. **84**, 1439 (1998).
[16] M. Stolka, J. F. Janus, and D. M. Pai, J. Phys. Chem. **88**, 4707 (1984).
[17] S. Barth, P. Müller, H. Riel, P. F. Seidler, W. Riess, H. Vestweber, and H. Bässler, J. Appl. Phys. **89**, 3711 (2001).
[18] W. Helfrich, in *Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. Labes, and A. Weissberger (Wiley, New York, 1967), Vol. III, p. 1.
[19] J. Yang and J. Shen, J. Appl. Phys. **84**, 2105 (1998).
[20] J. Shen and J. Yang, J. Appl. Phys. **83**, 7706 (1998).